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ning of each regular issue of the PCT Gazette.



WO 01/34310 A1

(54) Title: PROCESS FOR THE NON-GALVANIC TIN PLATING OF COPPER OR COPPER ALLOYS

(57) Abstract: The invention describes a process for non-galvanic tin plating of copper and copper alloys by precipitation of tin from methanesulphonic acid and tin-containing electrolytes, containing a complexing agent. In describing a process by which a durable tin layer which can be soldered is created, which, at the same time, prevents liberation of the base material, this invention discloses that the electrolytes have at least one foreign metal added to form a diffusion barrier in the tin layer.

Title: Process for the non-galvanic tin plating of copper or copper alloys

The invention deals with a process for the non-galvanic tin plating of copper or copper alloys by precipitating tin from a tin-containing electrolyte, consisting of methanesulphonic acid and a complexing agent.

Non-galvanic tin precipitation is known from the current state of the art and is commonly used, based both on acidic and alkaline electrolytes. Primarily, copper and copper alloys are tin plated in an ion exchange process, for example pipes, pipe sections and fittings for cold and hot water, battery posts, sanitary connectors as well as conductor frames. As the source of the tin for the electrolytes especially bivalent tin salt is used, such as for example tin chloride, tin sulfate, tin tetrafluoroborate or tin methanesulphonate.

The formation of non-galvanically precipitated tin layers on copper and copper alloys is effected by the exchange of copper for tin atoms, whereby the removal of the copper is made possible by a complexing agent.

A generic process is described in DE 197 49 382 A1. The process described there refers to the tin plating of pipes, pipe sections and fittings of copper or a copper alloy by the chemical precipitation of a tin layer. Methanesulphonic acid, tin methanesulphonate, a complexing agent as well as a wetting agent are suggested as electrolyte.

The tin layers produced with the tin precipitation processes known heretofore only grow until no more surface copper can pass through the porous tin layer. The achievable layer thickness is therefore limited to a maximum of 2 μm . The disadvantage is that a diffusion of metals from the base material, especially of alloy components, can occur which may lead to undesirable effects. For example, copper of a potable water pipe may dissolve and diffuse through the tin and can enter the water, which may have effects detrimental to health. Also, the liberation of lead and zinc from brass base materials, for example, can not be prevented by the precipitation of a generic tin layer. In addition, difficulties with soldering of the surface of tin plated base materials due to the diffusion are a disadvantage.

In order to avoid the above disadvantages it is the purpose of the invention to devise a process for the non-galvanic tin plating of copper or copper alloys by which a durable tin layer which can easily be soldered can be produced which, at the same time, prevents the liberation of the basic material.

5 As a solution it is proposed by the invention that at least one foreign metal is added to the electrolyte to form a diffusion barrier in the tin layer.

With the process described in the invention, a tin bath is suggested for the formation of a tin layer by chemical precipitation, which contains at least one foreign metal. The addition of foreign metals to the tin bath achieves an advantageous suppression of the diffusion processes, and thus a diffusion barrier
10 is built which prevents the liberation of metals from the base material to a large extent. The advantages thus gained are good soldering characteristics at the surface and good durability of the tin layer.

The formation of a tin layer by the above process therefore not only
15 creates the possibility to produce effective corrosion protection but, moreover, by the use of foreign metals a diffusion-stable tin layer is produced which prevents the liberation of materials from the base layer to a large extent. This is an advantage especially in view of the copper liberation from potable water carrying copper tubing. However, an out-diffusion of lead and zinc from basic brass
20 materials is prevented by a diffusion-stable tin layer.

In accordance with one feature of the invention, a metal of the group silver, bismuth, nickel, titanium, zirconium and indium is suggested as the foreign metal, whereby the use of indium has shown to be especially effective. For the formation of a diffusion barrier within the tin layer, at least one of the above
25 metals is added to the tin bath as a foreign metal.

In accordance with an additional feature of the invention, thiourea and/or its derivative is used as the complexing agent. Thiourea as the complexing agent enables the liberation of positively charged copper ions. A copper thiourea complex forms which is soluble in electrolytes at a temperature of $>28^{\circ}\text{C}$. As a
30 result of the complexing of the copper, its potential compared to that of tin is reduced. The then more noble tin precipitates, forming a layer of tin on the copper. The liberated copper ions concentrate in the electrolyte, whereby at a

copper concentration above 7 g/l economical working is no longer possible since at these concentrations tin is no longer precipitated at satisfactory rates. It is therefore suggested to remove the copper by precipitation of the copper-thiourea compounds in solution in the electrolyte. In this manner, a substantial increase in the useful life of the tin bath may be achieved. The precipitation of the copper-thiourea compounds can be achieved by means of another feature of the invention by filtration.

For the application of the non-galvanic precipitation of diffusion-stable tin layers in accordance with the invention a tin bath is of advantage, which preferably contains the following components:

1. A source of tin,
preferably a bivalent tin salt, for example tin methanesulfonate,
with 1 to 30 g/l of tin in the tin bath;
2. An acid,
preferably methanesulphonic acid with 5 to 200 g/l in the tin bath,
whereby the tin bath assumes a pH value of 0 to 3;
3. A complexing agent,
preferably thiourea or a derivative in quantities of 10 to 200 g/l;
4. A wetting agent in quantities of 1 to 10 g/l;
5. At least one foreign metal,
preferably a metal in the group Ag, Bi, Ni, Ti, Zr and In in a proportion of
1 to 500 mg/l in the tin bath.

To apply the process described in the invention, a working temperature of the tin bath of 35 to 80°C is suggested. In addition, already known measures common to the state of the art can be taken when using the process described. This includes, for example, rinsing, pickling and drying of the work pieces.

Further details regarding the invention follow from the examples below in each of which an electrolyte composition is suggested.

Example 1

	Thiourea	100 g/l
5	Methanesulphonic acid	100 g/l
	Tin methanesulphonate	5 g/l tin
	Wetting agent	5 g/l
	Bismuth	30 mg/l

10 **Example 2**

	Thiourea	100 g/l
	Methanesulphonic acid	100 g/l
	Tin methanesulphonate	15 g/l tin
15	Wetting agent	3 g/l
	Antioxidant	5 g/l
	Titanium	5 mg/l

Example 3

20	Thiourea	120 g/l
	Methanesulphonic acid	140 g/l
	Tin methanesulphonate	15 g/l tin
	Wetting agent	5 g/l
25	Antioxidant	5 g/l
	Indium	50 mg/l

The process described by the invention makes it possible to produce diffusion-stable tin layers by means of chemical precipitation, whereby the diffusion barrier generated by the addition of foreign metals prevents the liberation of metals from the base materials in an advantageous manner. In addition, by using thiourea as complexing agent it becomes possible to remove the

copper ions liberated from the copper from the electrolyte by filtration, and thus to achieve a substantially extended useful life. Furthermore, in this manner a substantial acceleration of the process is achieved.

Claims

1. Process for non-galvanic tin plating of copper and copper alloys by precipitation of tin from methanesulphonic acid and tin-containing electrolytes, containing a complexing agent, characterized by the electrolyte having at least one foreign metal added in order to build a diffusion barrier in the tin layer.
2. A process in accordance with claim 1, characterized by a metal of the group Ag, Bi, Ni, Ti, Zr and In being used as the foreign metal.
3. A process in accordance with claims 1 and 2, characterized by thiourea and/or its derivative being used as a complexing agent.
4. A process in accordance with one of the preceding claims, characterized by the electrolytes being reconditioned by having the copper in solution removed through precipitation of the copper-thiourea compound.
5. A process in accordance with claim 4, characterized by the copper-thiourea compound being filtered out.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/30983

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B05D 1/18
US CL : 427/430.1, 436, 437

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 427/430.1, 436, 437

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 10-245683 A (SHODA) 14 September 1998, abstract.	1-2
Y	US 5,266,103 A (UCHIDA et al.) 30 November 1993, col. 4, line 60-col. 5, line 42.	1-2
A	US 5,217,751 A (KING et al.) 08 June 1993.	1
A	US 5,160,422 A (NISHIMURA et al.) 03 November 1992.	1
A	EP 0 715 003 A1 (SAKURAI et al.) 05 June 1996.	1

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/30983

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claim Nos.: 3-5
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/30983

Continuation of B. FIELDS SEARCHED Item 3: EAST: USPAT, EPO, JPO, DWPI, IBM TDB

search terms: methanesulfonic acid, tin, copper, plating, non-galvanic, thiourea, complexing agent, precipitate, electrolyte